

## CATALYTIC HYDROCRACKING OF COAL LIQUIDS

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### Introduction

The conversion of coal to gasoline involves removal of mineral matter, sulfur, nitrogen and oxygen. This is well illustrated in Table I which compares the composition of a coal and gasoline. In addition the hydrogen-to-carbon atomic ratio in gasoline is approximately double that in the coal so that large amounts of hydrogen must be added. Coal is a solid from which very little volatile material is obtained until cracking temperatures are reached, whereas gasoline boils in a relatively low temperature range. Thus, the large, complex coal molecules must be broken down into smaller volatile compounds.

The coal-to-gasoline process consists broadly of two essential steps as illustrated in Table II. The first step is to convert at least a portion of the coal to liquid product. The processes suggested for this range from simple pyrolysis to non-catalytic hydrogenation to catalytic hydrogenation, all with and without a liquid vehicle. A small amount of gasoline range material may be produced in this step, but the liquid product is usually largely higher boiling. Some of these heavy liquids may be recycled to the liquefaction step, but the remainder must be upgraded to the gasoline range by a subsequent refining step such as hydrocracking, which may or may not be followed by reforming. In this paper the results of catalytic hydrocracking (with and without previous hydrofining) of a 400-700°F fraction of liquid obtained through the non-catalytic hydrogenation of coal are discussed. Much work has been done on hydrocracking of various coal

liquids<sup>1-14,16,17</sup> and it should be borne in mind that the results are highly dependent on the coal used initially and the method of liquefaction as well as the catalyst used and the conditions employed. An excellent review of hydrogenation of coal and tar was issued by the Bureau of Mines in 1968.<sup>18</sup>

#### Experimental

A simplified schematic diagram of the hydrocracking unit is shown in Figure 1. The hydrogen treat gas rate was maintained at approximately 8000 SCF per barrel of feed. The hydrofined feedstock was spiked back up to its original nitrogen and sulfur levels with suitable nitrogen and sulfur containing compounds which react quickly at the conditions employed to give ammonia and hydrogen sulfide. This was done in order to simulate commercial conditions of some hydrocracking units wherein the liquid and gas product from the hydrofiner may be fed directly to the hydrocracker without previous scrubbing.

The properties of the two feedstocks are listed in Table III. The aromatics contents of the 400°F+ material are considerably higher than those of typical petroleum hydrocracking feedstocks<sup>15</sup> and also higher than those reported for some of the coal liquids<sup>14</sup>. In addition to the reduction of the organic nitrogen content a good deal of hydrogen addition was accomplished by the hydrofining. A large part of the indicated conversions of 400°F+ material to 400°F- was probably due to hydrogenation of aromatic compounds boiling slightly above 400°F to hydroaromatic and naphthenic compounds boiling slightly below 400°F.

#### Results and Discussion

It was found that, over the range of conversions studied, the results for both the raw (unhydrofined) feedstock and the hydrofined feedstock could be correlated with first order kinetics, i.e.,

$$\frac{-d(400^{\circ}\text{F}+)}{dt} = k(400^{\circ}\text{F}+) \quad (1)$$

This is illustrated in Figure 2 where the holding time was taken as the reciprocal of the liquid hourly space velocity in weights of liquid per weight of catalyst per hour. Since the raw feedstock was more resistant to hydrocracking, the kinetic data were obtained at a different temperature for each feedstock. It should be borne in mind that we do not have simple pure compounds here, but complex mixtures; thus, the correlations with first order kinetics are probably fortuitous. At least inference of a mechanism from this correlation is probably unwarranted.

Mass spectral data, however, made it possible to follow the changes in concentration of specific molecular weights. Figure 3 shows a first-order plot for  $C_{14}H_{10}$ , which consists of anthracene and phenanthrene and which was the highest molecular weight present in the feed in any appreciable concentration. In all probability no hydrocracking of anthracene or phenanthrene occurs as a first step and the kinetics here represent the rate of the first hydrogenation step.

Table IV shows that prior hydrofining has a beneficial effect on the hydrocracking rate. As mentioned before, the hydrofined feed was spiked back up to the original nitrogen and sulfur level of the raw feed.

Experiments have shown that even the hydrofined coal liquid fraction is considerably more resistant to hydrocracking than are petroleum feedstocks. This is probably due in part to the higher total nitrogen content. This view is somewhat reinforced by the results shown in Table V. This table compares the conversions obtained on the respiked hydrofined feed with those obtained on the unspiked 400°F+ material recovered from the product. The higher activity with the latter feed is probably also partially due to its higher hydrogen content.

The beneficial effects of the prior hydrofining are further illustrated in Figure 4 which shows the Arrhenius temperature dependence of the first order rate constants for hydrocracking both feeds. At 650°F the rates for the two feeds are approximately the same, but too low to be of interest. The hydrofined

feed has a higher apparent energy of activation so that, as the temperature is increased, the benefit of hydrofining increases. As mentioned earlier, some boiling point conversion was obtained in the hydrofining operations, but this was probably largely due to hydrogenation of aromatic compounds boiling slightly above 400°F to hydroaromatic and naphthenic compounds boiling slightly below 400°F. In the case of the raw feed some conversion of this type also occurs in the hydrocracking operation.

Increasing hydrocracking pressure also has a greater effect on the rate constant with hydrofined feed than with the raw feed. This is shown in Table VI. Increasing the pressure from 1500 psig to 3000 psig approximately tripled the rate with the hydrofined feed whereas the rate with the raw feed was approximately doubled.

Figure 5 shows the change in concentration of certain specific molecular weights and carbon numbers as compared to boiling point conversion and holding time for both the raw feed and the hydrofined feed. For the hydrofined feed the boiling point conversion which is plotted is the sum of that obtained in hydrofining and hydrocracking although the holding times are only those for hydrocracking. The completely aromatic compounds such as naphthalene,  $C_{10}H_8$ , and anthracene and/or phenanthrene,  $C_{14}H_{10}$ , were completely converted to saturated and partially saturated compounds in the hydrofining operation. The total concentration of  $C_{10}$  compounds remains relatively constant over a wide range of holding time and conversion, indicating that  $C_{10}$  compounds are being formed from higher molecular weight compounds at approximately the same rate that they are consumed to form lower molecular weight compounds. Some of the specific molecular weights have maxima in their concentration vs. holding time curves, indicating that they are initially produced faster than they are consumed. Benzene is produced in much higher-than-equilibrium concentrations, indicating that a considerable amount of cracking of higher molecular weight compounds occurs before they are completely saturated.

Table VII shows analyses of some fractions of the naphtha from a hydrocracking product from the hydrofined feed. The paraffin content is very low except for the lowest boiling cut which is itself only a small fraction of the naphtha. The high naphthene content should make this naphtha an excellent feed for catalytic reforming.

These studies have shown that higher boiling liquids obtained in coal liquefaction can be catalytically hydrocracked to the gasoline boiling range under reasonable conditions although more severe than those required for petroleum stocks. Prior hydrofining is beneficial and the advantage increases with increasing hydrocracking temperature and pressure. The higher resistance to hydrocracking of coal liquids is probably largely due to higher nitrogen content. Mass spectral data indicate that a fair amount of cracking of higher molecular weight compounds occurs before they are completely saturated. The naphtha products should be excellent feedstocks for reforming.

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Table I  
Comparison of Coal and Gasoline

	<u>Coal</u>	<u>Gasoline (From Coal)</u>
Mineral Matter, Wt. %	~13	0
Sulfur, Wt. %*	3.4	Trace
Nitrogen, Wt. %*	1.3	Trace
Oxygen, Wt. %*	10.6	Trace
Hydrogen, Wt. %*	5.6	12-13
Carbon, Wt. %*	79.1	87-88
H to C Atomic Ratio	0.85	1.6-1.8
Boiling Range, °F	N.A.	160-400

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\* Dry, Mineral Free

Table II

Process Steps

1. Conversion of a portion of the coal to liquid product. Some gasoline range material but most heavy liquid.
  - Pyrolysis
  - Hydrogenation
2. Upgrading of heavy liquids to gasoline range.
  - Hydrocracking
  - Catalytic reforming

Table III  
Feed Stock Properties

	<u>Unhydrofined</u>	<u>Hydrofined</u>
Carbon, Wt. %	89.84	89.30
Hydrogen, Wt. %	8.33	10.45
Sulfur, ppm	520	-
Nitrogen, ppm	3400	5
Specific Gravity	1.0060	0.9402
400°F-, Wt. %	6.0	18.6
Sulfur, ppm	280	-
Nitrogen, ppm	2800	-
Paraffins, Vol. %	0.0	2.4
Naphthenes, Vol. %	26.5	50.1
Aromatics, Vol. %	73.0	47.5
400°F+, Wt. %	94.0	81.4
Sulfur, ppm	460	-
Nitrogen, ppm	3500	-
Saturates, Vol. %	2.7	22.8
Aromatics, Vol. %	97.3	77.2

Table IV

Effect of Hydrofining

750° F

	<u>Raw Feed</u>	<u>Hydrofined Feed</u>
Total Nitrogen, ppm	3400	3400
Organic Nitrogen, ppm	3400	5
First Order Rate Constant, Hr <sup>-1</sup>	0.25	0.46

Table V

Effect of Total Nitrogen Content

675°F

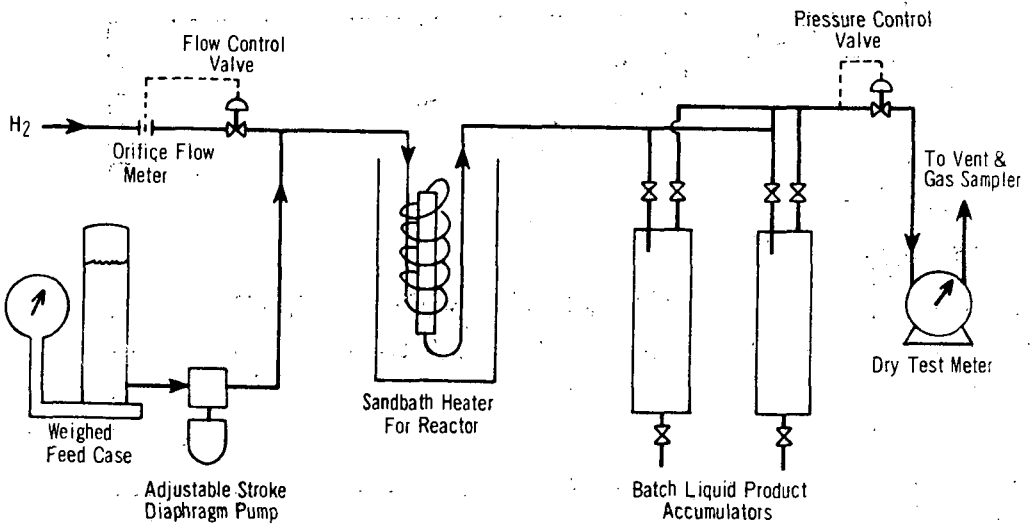
	<u>Hydrofined Feed</u>	<u>400°F+ Material Recovered from Hydrocrackate</u>
Total Nitrogen, ppm	3400	6
Organic Nitrogen, ppm	5	6
Hydrogen, Wt. %	10.45	11.00
400°F+ Conversion, Wt. %	14	85

Table VI  
Effect of Pressure

	<u>Raw Feed</u>	<u>Hydrofined Feed</u>
Temperature, °F	700	650
First Order Rate Constant, Hr <sup>-1</sup>		
at 1500 psig	0.13	0.041
at 3000 psig	0.24	0.12

Table VII  
Analyses of Naphtha Cuts  
Hydrofined Feed, 30% Total Conversion

<u>Boiling Range, °F</u>	<u>IBP-160</u>	<u>160-300</u>	<u>300-350</u>	<u>350-400</u>
Wt. % of Naphtha	3.9	31.0	14.3	50.8
Benzene	23.1	10.3	0.4	
Toluene		8.0	1.5	
C <sub>8</sub> Benzene		9.3	6.0	
C <sub>9</sub> Benzene		1.6	10.7	
C <sub>10</sub> Benzene			3.1	
C <sub>11</sub> Benzene			0	
Indan		0.1	15.8	
Naphthenes	61.9	68.9	35.0	
Paraffins	15.0	0.9	0	
Condensed Naphthenes		0.9	27.5	
Naphthalenes			0	
	100.0	100.0	100.0	



SIMPLIFIED FLOW DIAGRAM OF BENCH UNIT

FIGURE 1

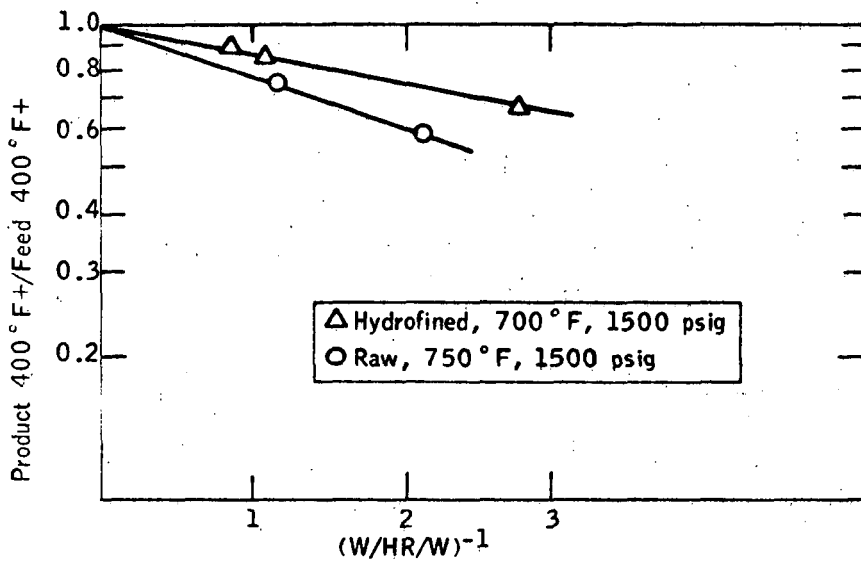


Fig. 2

HYDROCRACKING OF 400-700° F CUT

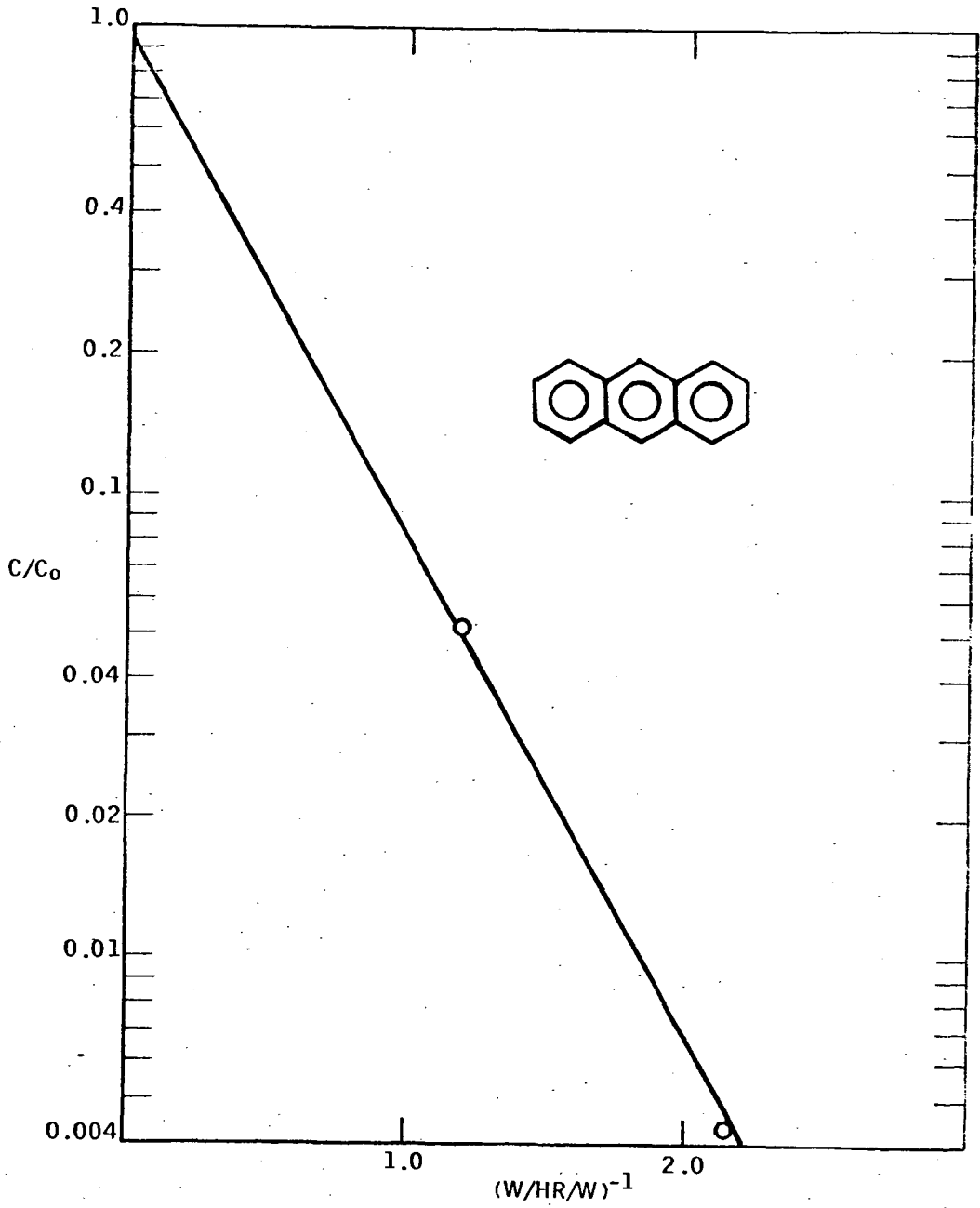


Figure 3

ANTHRACENE IN HYDROCRACKING RAW 400-700°F  
750°F, 1500 psig

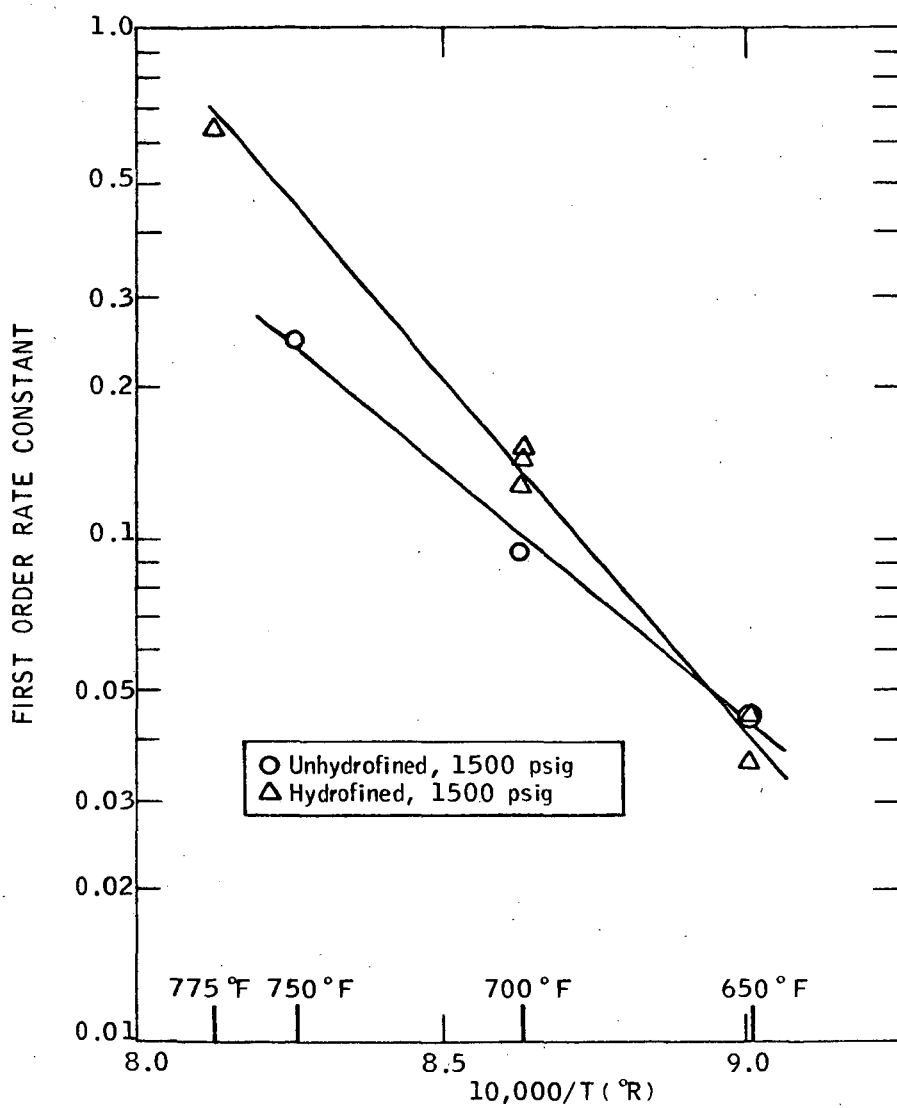


Fig. 4  
HYDROCRACKING OF 400-700 °F DISTILLATE

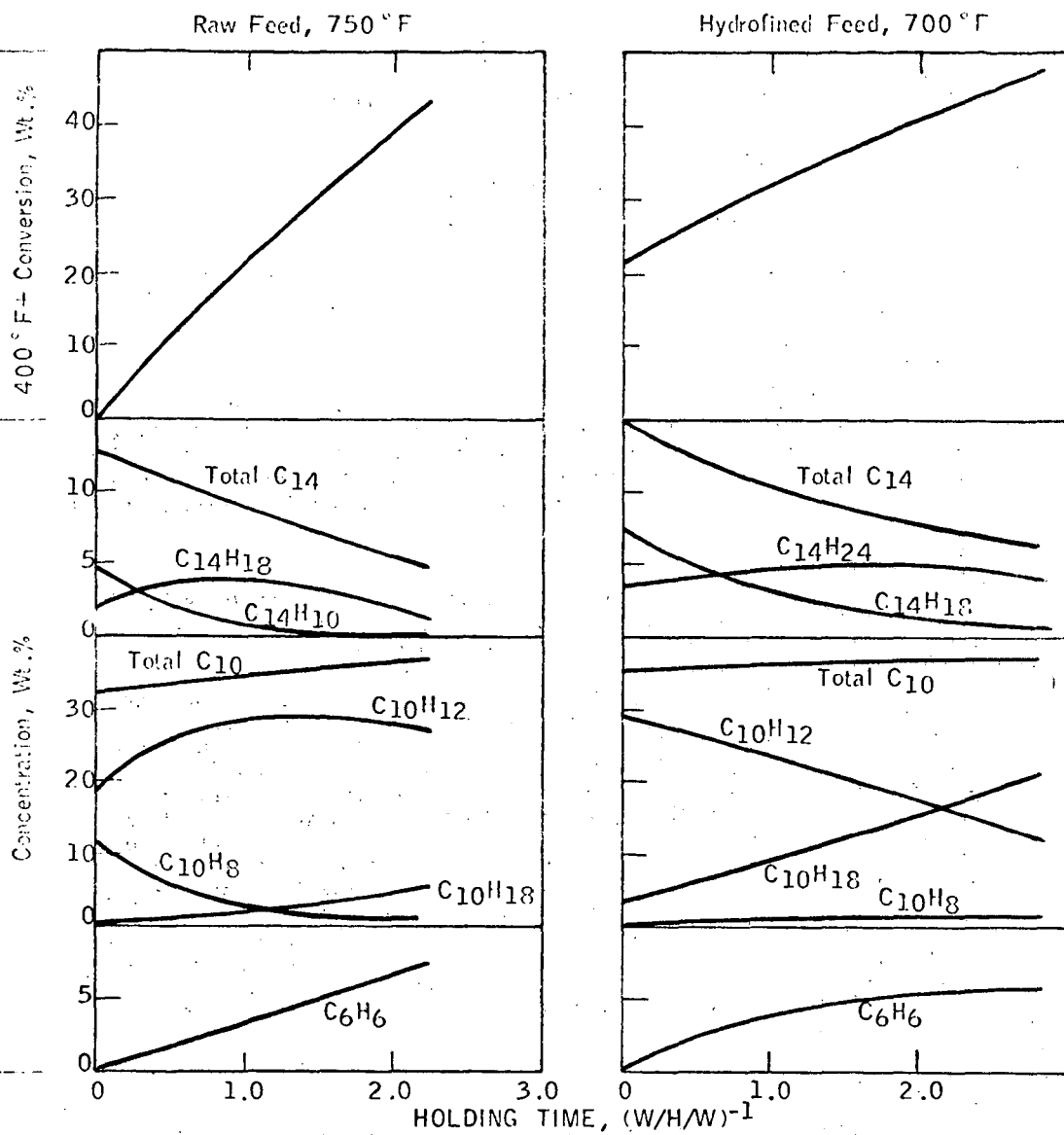


Fig. 5

HYDROCRACKING OF 400-700°F CUT